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Test Area North (TAN) at the Idaho National Engineering and Environmental Laboratory (INEEL) is the site of a large trichloroethene (TCE) plume resulting from the historical injection of wastewater into the Snake River Plain Aquifer. The TAN Record of Decision (ROD) selected pump and treat as the final remedy and included a contingency for post-ROD treatability studies of alternative technologies. The technologies still under consideration are in situ bioremediation, in situ chemical oxidation, and natural attenuation. Both anaerobic and aerobic laboratory microcosm studies indicate the presence of microorganisms capable of chloroethene degradation. Field data indicate that TCE concentrations decrease relative to tritium and tetrachloroethene indicating an as yet unknown process is contributing to natural attenuation of TCE. Several methods for analyzing the field data have been evaluated and important limitations identified. Early results from the continued evaluation of the three alternative technologies suggest the combined approach of active remediation of the source area (in situ bioremediation and/or chemical oxidation replacing or augmenting pump and treat) and natural attenuation within the dissolved phase plume may be more cost and schedule effective than the base case pump and treat.

INTRODUCTION

Natural attenuation of TCE is being evaluated as a component of remediation for a nearly 2-mile long plume in a basalt aquifer at the Idaho National Engineering and Environmental Laboratory. The record of decision identified natural attenuation and four other innovative technologies for evaluation of their potential to replace or augment pump and treat. During the study of natural attenuation, the significance of intrinsic anaerobic reductive dechlorination at the site was investigated. While it is occurring to a limited extent, the anaerobic process does not seem to account for a major portion of the attenuation apparent in the field data. Several different methods for analyzing field data were evaluated in an attempt to understand the transport processes affecting TCE in the large, aerobic portion of the plume. The applications and limitations of three different first-order methods are discussed in this paper. Perhaps most important at this site, the presence of the co-contaminants, tritium and PCE, has facilitated the evaluation of attenuation under aerobic conditions through the method of Wiedemeier et al. (1996). Although a mechanism has not been identified, this analysis suggests TCE degradation is occurring in the aerobic portion of the plume and provides a preliminary rate estimate indicating that the degradation may be significant relative to the restoration time frame of 100 years specified in the Record of Decision for the site. A more complete presentation of the work discussed in this paper can be found in Sorenson et al. (1999).

SITE BACKGROUND

The Idaho National Engineering and Environmental Laboratory (INEEL), a facility operated by the United States Department of Energy, is located near the northern edge of the Eastern Snake River Plain in Idaho. Groundwater contamination in the Snake River Plain Aquifer (SRPA) resulting from operations at Test Area North (TAN) was first detected in 1987 during routine monitoring of the drinking water supply wells. Subsequent sampling of aquifer monitoring wells confirmed the presence of tetrachloroethene (PCE), trichloroethene (TCE), 1,2-dichloroethene (DCE), tritium, strontium-90, cesium-137, and uranium-234 above risk-based concentrations.

The TSF-05 injection well (Figure 1) has been identified as the source of groundwater contamination. Liquid waste was disposed in the well directly to the SRPA between the mid-1950s and 1972. The wastes included organic, inorganic, and low-level radioactive wastes added to industrial wastewater and sanitary sewage. Characterization of sludge that remained in the well in 1990 revealed that the sludge was comprised of greater than 2% TCE and contained high levels of radionuclides (Kaminsky et al., 1994). Groundwater monitoring determined that the TCE plume emanating from the injection well extends approximately 2740 m (9000 ft) to the southeast. Vertically, the contamination appears to be isolated between the water table at 64 m (210 ft) below ground surface and a continuous, areally extensive sedimentary interbed located about 125 m (410 ft) below ground surface at well TSF-05.

The SRPA is composed of a complex layering of fractured basalt flows intercalated with sedimentary interbeds deposited during prolonged periods of volcanic quiescence. Depth to water in the vicinity of TAN is approximately 64 m (210 ft). Groundwater flow is controlled primarily by the distribution of interflow zones consisting of highly vesicular, fractured basalt formed when the base of a new lava flow cooled rapidly as it was deposited on an existing,

weathered basalt surface (Mundorff et al., 1964; Garabedian, 1986; Whitehead, 1992). On a small scale this can result in highly preferential groundwater flow, but beyond the scale of a single basalt flow (i.e., a few hundred to thousands of meters), groundwater flow can generally be predicted adequately with equivalent porous medium models because fractures within basalt flows and intersections with other basalt flows provide significant hydraulic communication among the interflow zones (Garabedian, 1987; Whitehead, 1992). The average groundwater velocity at TAN appears to be in the range of 0.11 to 0.15 m/day (0.35 to 0.50 ft/day) (Sorenson et al., 1999).

FIELD DATA ANALYSIS

The highest concentrations of chlorinated ethenes (and radionuclides) are still present at the former injection well (TSF-05) some 25 years after disposal in the well has ceased. This indicates that a continuing, fixed source of TCE is present in the area immediately around the former injection well. In the absence of a secondary source, the most contaminated water would have migrated downgradient following the regional groundwater flow. One of the first indications that some form of natural attenuation might be important at TAN is the fact that TCE concentrations measured over time at wells along the plume axis downgradient of Well TSF-05 are not increasing (Figure 2), despite the fact that a residual source of TCE near the former injection well has maintained high groundwater concentrations in that area. Given the presence of the 125-m (410-ft) interbed and a continuous residual source of TCE, conservation of mass requires that the TCE plume grow in aerial extent unless some process is occurring which removes mass from the plume at least at the rate mass is added at the source. However, as shown in Figure 2, concentrations in the upgradient portion of the plume have not been observed to increase, nor has the plume width or extent been observed to increase since monitoring of the plume began in 1990. This suggests that one or more natural attenuation processes may be removing mass from the plume.

The natural attenuation mechanisms that have been evaluated at TAN include anaerobic reductive dechlorination, aerobic degradation through an as yet undetermined process, and dispersion. Sorption was considered only briefly as laboratory testing has shown that TCE has very little affinity for basalt (Ingram et al., 1998). This is primarily due to the absence of organic material. Dispersion describes the extent to which TCE-contaminated groundwater mixes with, and is therefore diluted by, surrounding clean groundwater. Dispersion does not actually remove mass from the plume, but at the fringes of the plume it dilutes the contaminated groundwater so that TCE concentrations fall below detection limits or other levels of concern.

Anaerobic Reductive Dechlorination

The data collected at TAN to date strongly suggest that anaerobic reductive dechlorination is in fact occurring. The conditions in the aquifer near TSF-05 are appropriate for anaerobic reductive dechlorination. Dissolved oxygen (DO) data were collected in 1996 from several wells in the upgradient portion of the plume. It was found that the DO was below 1 mg/L as far as 150 m (500 ft) downgradient of well TSF-05 indicating that anaerobic conditions exist. Degradation of the sanitary sewage with TCE has probably depleted the oxygen around TSF-05. The sewage and other organic compounds co-disposed with TCE may be providing substrate for microbes which are responsible for the reductive dechlorination of TCE; however, characterization data suggest that these compounds are present only within about 23 m (75 ft)

from well TSF-05. Finally laboratory studies have confirmed that microbes present in the vicinity of well TSF-05 are capable of TCE degradation under anaerobic conditions.

Further evidence for dechlorination at TAN is seen in the relative concentrations of chlorinated hydrocarbons at wells in the upgradient portion of the plume (Figure 3). TCE is the primary contaminant in all of the wells; however, the relative concentrations of contaminants are not constant and may provide information regarding the fate of TCE. The fact that DCE, the second most prevalent chlorinated hydrocarbon at well TSF-05, is found primarily around the source and downgradient of the source, and that the isomer cis-1,2-DCE exhibits concentrations greater than trans-1,2-DCE and 1,1-DCE in every well at TAN where they have been detected suggests that the primary source of DCE is the reductive dechlorination of TCE. Figure 3 shows that DCE is relatively constant as a percentage of total contamination within 15 m (50 ft) of well TSF-05, and then decreases downgradient. It appears DCE is primarily generated near wells TSF-05, TAN-25, and TAN-26 where electron donors (substrate) are readily available. Finally, other possible products of reductive dechlorination including vinyl chloride and ethene have been detected. Vinyl chloride has been detected consistently in the off-gas of an air stripper treating groundwater from wells TSF-05 and TAN-25. Ethene has been detected in low concentrations in the groundwater in wells TSF-05 and TAN-27. These data indicate that it may be possible to achieve complete dechlorination of TCE at TAN.

While reductive dechlorination is occurring, it appears to be limited to the immediate vicinity of Well TSF-05 due to the lack of dissolved organic carbon (based on the distribution of DCE and the increasing dissolved oxygen concentrations downgradient). Intrinsic reductive dechlorination, therefore, is apparently not sufficient to restore the groundwater at TAN in a reasonable time frame. The fact that it is occurring and is probably carbon-limited, however, indicates that enhanced in situ bioremediation through reductive dechlorination may be a cost-effective technology for remediating the source area. A 1-year field evaluation of this technology is being conducted in the area between Wells TSF-05 and TAN-29 from November 1998 to November 1999.

Aerobic Attenuation

After evaluating anaerobic reductive dechlorination of TCE, the possibility was considered of an aerobic degradation mechanism as a potential means to reconcile the apparent stability of the plume (Figure 2) with the relatively small reductive zone. In order to investigate this possibility at TAN, evidence for degradation was sought in that portion of the TCE plume downgradient from the reductive zone, which was assumed to extend from the former injection well to Well TAN-28. The remainder of this paper focuses on the use of three methods presented in the literature to evaluate and estimate TCE degradation at TAN based on groundwater concentrations measured at monitoring wells and illustrates some important limitations. All three methods rely on the assumption that first-order kinetics can be used to model degradation. This is a common assumption (Rifai et al., 1995) that has been found to be appropriate at many sites (e.g., Rifai et al., 1995; Weaver et al., 1996; Ellis, 1996; Wilson et al., 1996; Wiedemeier et al., 1996; Aronson and Howard, 1997). It has been noted that first-order kinetics do not account for the limitation of contaminant degradation rates by the presence of some compound other than the contaminant (Rifai, 1994).

Graphical Extraction. First-order decay of any compound is described by the equation

$$C = C_o e^{-kt} \qquad (1)$$

where C [M/L^3]is the concentration of the compound after elapsed time, t [T], C_o is the initial concentration, and k [T^{-1}]is the first-order decay constant. The first method for estimating degradation of a groundwater contaminant simply takes advantage of this equation which implies that when the natural logarithm of the ratio of the downgradient contaminant concentration to the concentration at an upgradient reference point is plotted as a function of the travel time between points, the slope of the resulting line is equal to the first-order decay constant, k. This has been called the graphical extraction method by Ellis (1996). Of course a groundwater velocity is required to plot the travel time between observation points. A constant value of 0.11 m/day (0.35 ft/day) is assumed here. The minimum value presented earlier is used so that the calculated travel time will be a maximum and the first order degradation rate estimate will be a conservative minimum. It is important to note, however, that the first-order "decay" constant estimated by this method includes the effects of all processes that cause contaminant concentrations to decrease along a flow path (e.g., dispersion, matrix diffusion, sorption, volatilization, and degradation). Thus, the estimate may or may not indicate the significance of degradation. Nevertheless, the method as applied at TAN is included as a point of comparison.

In Figure 4, 1997 groundwater monitoring data from 15 wells near the plume axis are plotted as described above. When wells were sampled more than once during the year, the average of the values observed was used. The reference point in the plot is Well TAN-28 because it is assumed to mark the downgradient extent of the reductive zone. The total first-order "decay" rate estimated from the plot is 2.3X10^{-4} per day, which is equivalent to an 8.3-year half-life. The R^2 value of 0.98 seems to support the use of a first-order representation of TCE attenuation at TAN. Again, it is emphasized that this estimate includes the effects of all processes that cause concentrations to decrease during downgradient transport. One implication of this fact is that the decay constant calculated by this method will never be zero unless contaminant concentrations are constant along a flow line which could only occur in a one-dimensional aquifer with no dispersion.

Buscheck and Alcantar Method. The second method for estimating contaminant degradation from groundwater concentration measurements was presented by Buscheck and Alcantar (1995). This method is slightly more sophisticated than graphical extraction because it incorporates information about dispersion and sorption with the intent of distinguishing these processes from degradation. The method makes use of a plot similar to Figure 4 except that the abscissa represents distance rather than travel time. The slope of the line, then, is equal to the decay constant divided by the groundwater velocity, k/v_x, because the travel time is the distance divided the groundwater velocity. As with graphical extraction, this method inherently assumes a constant groundwater velocity. Buscheck and Alcantar rearranged the solution of the one-dimensional transport equation including first-order decay presented by Bear (1979) to obtain the following equation for the first-order degradation rate, λ [T^{-1}]:

$$\lambda = \left(v_c / 4\alpha_x\right)\left(\left[1 + 2\alpha_x\left(k/v_x\right)\right]^2 - 1\right) \qquad (2)$$

where v_c [L/T] is the contaminant velocity, α_x [L] is the longitudinal dispersivity, k is the gross first-order degradation rate (as would be calculated from graphical extraction), and v_x [L/T] is the groundwater velocity.

Of course this approach assumes that reasonable estimates of longitudinal dispersivity and sorption (contaminant retardation) are available. The method development assumes volatilization is negligible. This is generally reasonable except in very shallow aquifers. Given these parameters and k/v_x obtained from the appropriate plot, a decay constant can be calculated

that is presumably due to contaminant degradation. Figure 5 illustrates the application of the method using the TAN 1997 groundwater monitoring data. Of course the first-order fit is good again because this is the same data as in Figure 4 plotted slightly differently. Using k/v_x from the figure, a groundwater velocity of 0.11 m/day (0.35 ft/day), a dispersivity of 20 m (66 ft) based on inverse numerical modeling of the tritium plume at the site, and a retardation factor of 1 (no sorption, $v_c = v_x$), the first-order degradation constant, λ, was estimated to be $2.4X10^{-4}$ per day, equivalent to a half-life of 8.0 years.

While the graphical extraction and Buscheck and Alcantar (1995) methods are useful for screening purposes, they require assumptions that may not be satisfied in many cases. The first assumption is that the plume is stable. Plume stability is established when the rate of contaminant mass removal by all natural attenuation processes is equal to the rate of contaminant addition at the source so that contaminant concentrations at individual monitoring points remain approximately constant. A second important assumption that applies to the Buscheck and Alcantar method is that transverse dispersivity is insignificant. Transverse dispersivity is essentially the parameter used to quantify the spreading of a plume. Of course the spreading of a plume contributes to the decrease in contaminant concentrations along the axis of the plume. So, while transverse dispersivity is usually less than longitudinal dispersivity, it generally is not insignificant as far as its effect on contaminant concentrations along a flow path. One manifestation of this issue in the Buscheck and Alcantar method is that the decay constant will never be zero unless the slope of Figure 5 is zero. As discussed in the graphical extraction method, this will almost never be true in a real aquifer regardless of whether degradation is occurring, largely because of the two- or even three-dimensional effect of transverse dispersivity. While it can be argued that if a plume is stable, the degradation rate must be non-zero, neglecting transverse dispersivity may result in significantly overestimating the rate.

Another difficulty with the use of longitudinal dispersivity in this approach is that its effect on the solution of equation 2 may be counter-intuitive. The rate estimate obtained from a given data set will actually increase with increased dispersivity because of the one-dimensional, steady-state assumptions. This is because under one-dimensional, steady-state conditions, increasing the longitudinal dispersivity will tend to spread higher concentrations further downgradient from the source, thereby increasing the contaminant concentration at a given observation point. That is, dispersivity in the Buscheck and Alcantar (1995) approach does not act as a natural attenuation mechanism that causes dilution in the plume, but instead increases the degradation rate, λ, required to reproduce the observed concentration decline. In a case with zero sorption, an infinitesimal dispersivity will result in the same degradation rate estimate as would be obtained for k from graphical extraction. Increasing the value of dispersivity will increase the rate estimate relative to graphical extraction as shown with the TAN data. In the end, if sorption is not significant, graphical extraction provides a more conservative rate estimate for degradation in the sense that it will not overestimate degradation as much. In cases where sorption is significant, the Buscheck and Alcantar approach will be more conservative than graphical extraction unless a high value for dispersivity is used.

Wiedemeier et al. Method. The third method used to estimate TCE degradation at TAN eliminates some of the concerns discussed for the other two methods through normalization of TCE concentrations by concentrations of a recalcitrant compound that is subject to the same multi-dimensional transport mechanisms. The method, described in Wiedemeier et al. (1996), estimates the degradation rate of a compound between two points on a groundwater flow path by

calculating a normalized (or corrected) concentration of the compound at the downgradient point through the equation:

$$C_{B,corr} = C_B\left(C_{T,A}/C_{T,B}\right) \qquad (3)$$

where $C_{B,corr}$ is the corrected concentration of the compound at downgradient point B, C_B is the observed concentration of the compound, $C_{T,A}$ is the observed concentration of an internal tracer at upgradient observation point A, and $C_{T,B}$ is the observed concentration of the internal tracer at point B. The corrected downgradient concentration of the contaminant, $C_{B,corr}$, and the observed upgradient concentration, C_A, can then be used in equation 1 to estimate a first-order decay constant that is independent of dispersion and dilution from recharge. The estimated constant will be independent of sorption and volatilization if the appropriate partitioning coefficients of the tracer are similar to those of the contaminant, or if these processes are insignificant.

The essence of the correction in equation 3 is that if the contaminant is not attenuated relative to the tracer between points A and B (i.e., the ratio of the contaminants is constant from point A to downgradient point B) then $C_{B,corr}$ will equal C_A and the decay constant from equation 1 will be zero. If the ratio of the contaminant to the tracer decreases from point A to point B, then $C_{B,corr}$ will be less than C_A, and a degradation rate can be estimated. The role of this ratio can be illustrated clearly through a slight modification of the approach presented by Wiedemeier et al. (1996). Letting the ratio of the contaminant concentration at a point, x, to the tracer concentration at point x be noted by C^*_x and the concentration at the upgradient reference point by denoted by C^*_A, then one can obtain the following equation (Sorenson et al., 1999):

$$\ln\left(C^*_x\right) = \left(k/v\right)x + \ln\left(C^*_A\right) \qquad (4)$$

This equation reveals that when the natural logarithm of the ratio of contaminant concentration to tracer concentration is plotted against distance along a flow path, the slope of the line is equal to the first-order degradation rate divided by the groundwater velocity. Note that if travel time is plotted as the abscissa, the slope is simply equal to the degradation rate. Now it is clear that the method presented by Wiedemeier et al. (1996) can be applied in a manner analogous to graphical extraction except that the contaminant concentrations plotted are normalized by tracer concentrations.

The fact that this method can discriminate contaminants for which concentration decreases are due only to dispersion and dilution from those that actually degrade is a major advantage over the other two methods. Of course, an appropriate tracer must be available in the plume. A tracer must meet three requirements to be useful for this method: 1) it must originate from the same source as the contaminant of interest (with the source terms being proportional), 2) it must be recalcitrant to degradation relative to the contaminant of interest, and 3) the differences in partitioning coefficients between the tracer and the contaminant must be understood and accounted for if necessary.

Two compounds at TAN, tritium and PCE, were used as tracers for evaluating the possibility of aerobic TCE degradation. Both compounds would be expected to be recalcitrant to aerobic degradation satisfying the second requirement. Tritium has a radioactive half-life of 12.3 years, but this can be easily accounted for using equation 2 with the estimated travel time between observation points. Tritium would not be subject to sorption or volatilization while TCE might be in some environments. The advantage of PCE as a second tracer is that it would sorb more readily to organic material in the aquifer than TCE and it is also volatile. The aquifer at TAN has almost no organic carbon and a depth to water of over 60 m (200 ft) so sorption and

volatilization of TCE would be expected to be insignificant. The use of both tritium and PCE as tracers allows this hypothesis to be tested and satisfies the third requirement.

As for the first requirement for internal tracers, both compounds were co-disposed with TCE and the residual source at Well TSF-05 was not disturbed between 1972 and 1990. Given this, it can be reasonably assumed that the relative magnitudes of the residual sources for the three contaminants remained the same during this period. The highest concentrations of all three contaminants in groundwater at TAN were located at TSF-05 in 1990 when the sludge removal occurred (Kaminsky et al., 1994). The possibility must be considered, however, that source characterization and remediation activities since 1990 have impacted the residual sources of the three compounds differently. Given an average groundwater velocity of 0.11 m/day (0.35 ft/day), contaminants from the source would have been expected to travel about 271 m (890 ft) from 1990 to 1997, so only data further downgradient than this were considered in the analysis. It should also be noted that the most downgradient data point for tritium appears anomalously high and was removed from further analysis. If the point were included it would result in a large decrease in the TCE to tritium ratio that would give an artificially high apparent degradation rate.

As implied by equation 4 and the subsequent discussion, attenuation of one compound relative to another can be evaluated simply by plotting the ratios of the two compounds at observation wells as a function of distance downgradient. Figure 6 illustrates the ratios of TCE to PCE and TCE to tritium (corrected for its half-life) at observation wells near the axis of the TAN plume. In this figure, 1997 groundwater monitoring data from the axial wells including and downgradient of TAN-39 were used. Again, a single value of 0.11 m/d (0.35 ft/day) was used for the groundwater velocity for correcting tritium concentrations as above. Data from 1994, 1996, and 1998 were included where available in addition to the 1997 data to demonstrate that the analysis is temporally, as well as spatially, consistent. It is quite clear from the figure that TCE is being attenuated relative to both of the other compounds. While a fair amount of scatter is apparent in the data (as would be expected in this setting), the first-order fits appear to be reasonable. Multiplying the slopes of the plots by the average groundwater velocity, the first-order degradation rate of TCE relative to PCE is estimated to be $8.5X10^{-5}$ per day, while the rate relative to tritium is estimated to be $1.2X10^{-4}$ per day. These correspond to half-lives of about 22 and 16 years, respectively.

The fact that TCE is attenuated more than PCE effectively rules out sorption as the primary attenuation mechanism for TCE as expected. Perhaps a more likely hypothesis is that an oxidative degradation mechanism is affecting TCE in the aerobic portion of the plume. While TCE is somewhat susceptible to oxidation, PCE is very resistant to oxidation under typical in situ conditions (Vogel et al., 1987; McCarty, 1996).

The above analysis indicated that TCE may be undergoing a 16 to 22-year half-life under aerobic conditions at TAN. Assuming a 20-year half-life, TCE concentrations would undergo a 96.9% decrease in addition to dispersive effects during the specified remedial time frame at TAN of 100 years (assuming the source were isolated or removed). Thus, intrinsic aerobic degradation of TCE appears to be occurring to a measurable and significant extent.

DISCUSSION

The evaluation of natural attenuation mechanisms at TAN has revealed that while reductive dechlorination of TCE is occurring, it is very limited in areal extent and it does not appear to be the dominant attenuation mechanism at the site. Somewhat surprisingly, TCE degradation in the large, aerobic portion of the plume appears to be a major contributor to the near-stability of the plume. Based on the attenuation of TCE relative to two other compounds, PCE and tritium, the degradation half-life for TCE in this part of the plume is conservatively estimated to be about 20 years. Using a higher, and probably more realistic, average ground water velocity would yield shorter half-life estimates (Sorenson et al., 1999). The total effective half-life for TCE due to all attenuation processes including dispersion was estimated to be about 8.3 years using graphical extraction.

In order to predict the long-term fate of an attenuating contaminant, one must incorporate both dispersion and degradation, so it may seem logical that the attenuation rate obtained from graphical extraction is appropriate to use for this purpose. Examination of the role of dispersion over time, however, reveals that the use of this rate will overpredict natural attenuation of a contaminant plume whose source is either removed or decreases with time. A numerical model was used to estimate the contribution of dispersion to attenuation at TAN. The aquifer transport properties were calibrated using the tritium disposal history and plume data (Sorenson et al., 1999). The TCE plume was then simulated for a 100-year period beginning with the TCE distribution in 1996 without degradation and assuming the residual source was removed to estimate the effect of dispersion alone on TCE concentrations.

Figure 7 illustrates the predicted maximum TCE concentration decline in basalt throughout the 100 years. The logarithm of the maximum concentration in a given year divided by the initial (1996) concentration is plotted in order to compare dispersion to a first-order process. If dispersion had a first-order effect over time, the slope of the decline in Figure 7 would be constant. It is clear, however, that the slope flattens out with time indicating that the concentration decrease due to dispersion slows with time. In this simulation, dispersion gives an apparent half-life for TCE of about 5 years during the first 22 years of transport, but then the equivalent half-life for the next 77 years of transport is about 34 years. Examination of the three-dimensional transport equation with first-order decay below reveals the reason for this behavior:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} - v_x \frac{\partial C}{\partial x} - kC \qquad (5)$$

where D_x is the longitudinal dispersion coefficient [L^2/T], D_y is the horizontal transverse dispersion coefficient, D_z is the vertical transverse dispersion coefficient, and y [L] and z [L] are the horizontal and vertical transverse distances, respectively.

It is apparent from equation 5 that the change in a contaminant's concentration over time due to dispersion depends on concentration gradients. Intuitively it seems clear that in a contaminant plume whose source has been removed, the concentration gradients will decrease as the plume moves downgradient and spreads due to dispersion. The rate of concentration decrease due to dispersion should be at a maximum at the initial time when the concentration gradients are at a maximum, and then the rate should decrease. While dispersion may play a significant role during the first several years of transport, it becomes less significant as time goes on and other processes may become much more important. The total attenuation rate will approach the degradation rate as the significance of dispersion decreases. Thus, distinguishing between dispersion and degradation when predicting long-term natural attenuation of groundwater contaminants will be very important.

CONCLUSIONS

Aerobic degradation of TCE that is slow relative to anaerobic reductive dechlorination, but that may be significant for remedial time frames, has been documented through analysis of field data in a basalt aquifer at the INEEL. The mechanism has not been determined, but the data collected to date appear to be consistent with biologically mediated oxidation. In addition to the overall oxidative geochemical conditions, the relatively conservative behavior of PCE and the lack of less chlorinated daughter products seem to rule out a reductive mechanism. Another potential mechanism for the observed degradation is hydrolysis. Although processes this slow can be difficult to study, their potential significance indicates that much more research in this area is warranted.

A method for normalizing contaminant concentrations based on internal tracers modified from Wiedemeier et al. (1996) was shown to distinguish dispersion from degradation, while the methods of graphical extraction and Buscheck and Alcantar (1995) do not. Transverse dispersivity is not accounted for in the other two methods and can have a significant effect on contaminant concentrations along a flow path. This effect is evident at TAN from the fact that the aerobic TCE half-life for degradation independent of dispersion was estimated to be about 20 years, while the estimated half-life including three-dimensional dispersive effects was about 8 years. The importance of distinguishing between degradation and dispersion when estimating natural attenuation rates was illustrated through the use of a numerical model as well as examination of the transport equation. Dispersion does not have a constant contribution to contaminant concentration decreases in a transient plume in which concentration gradients decrease over time. Thus, the contribution of dispersion to natural attenuation in a stable plume with an ongoing residual source is probably greater than it will be at some later time when the residual source is removed and gradients decrease.

Perhaps most important for TAN is the fact that TCE concentrations in groundwater would be predicted to decrease by 97% in 100 years using the estimated 20-year half-life, even without dispersion. The effect of transverse dispersion would lower these concentrations further and could be estimated either using the numerical model, or perhaps by using a two-dimensional analytical solution. Thus, if the TCE residual source is contained or actively treated, natural attenuation may provide a viable remedial solution for a significant portion of the TAN plume, despite the fact that it is predominantly aerobic.

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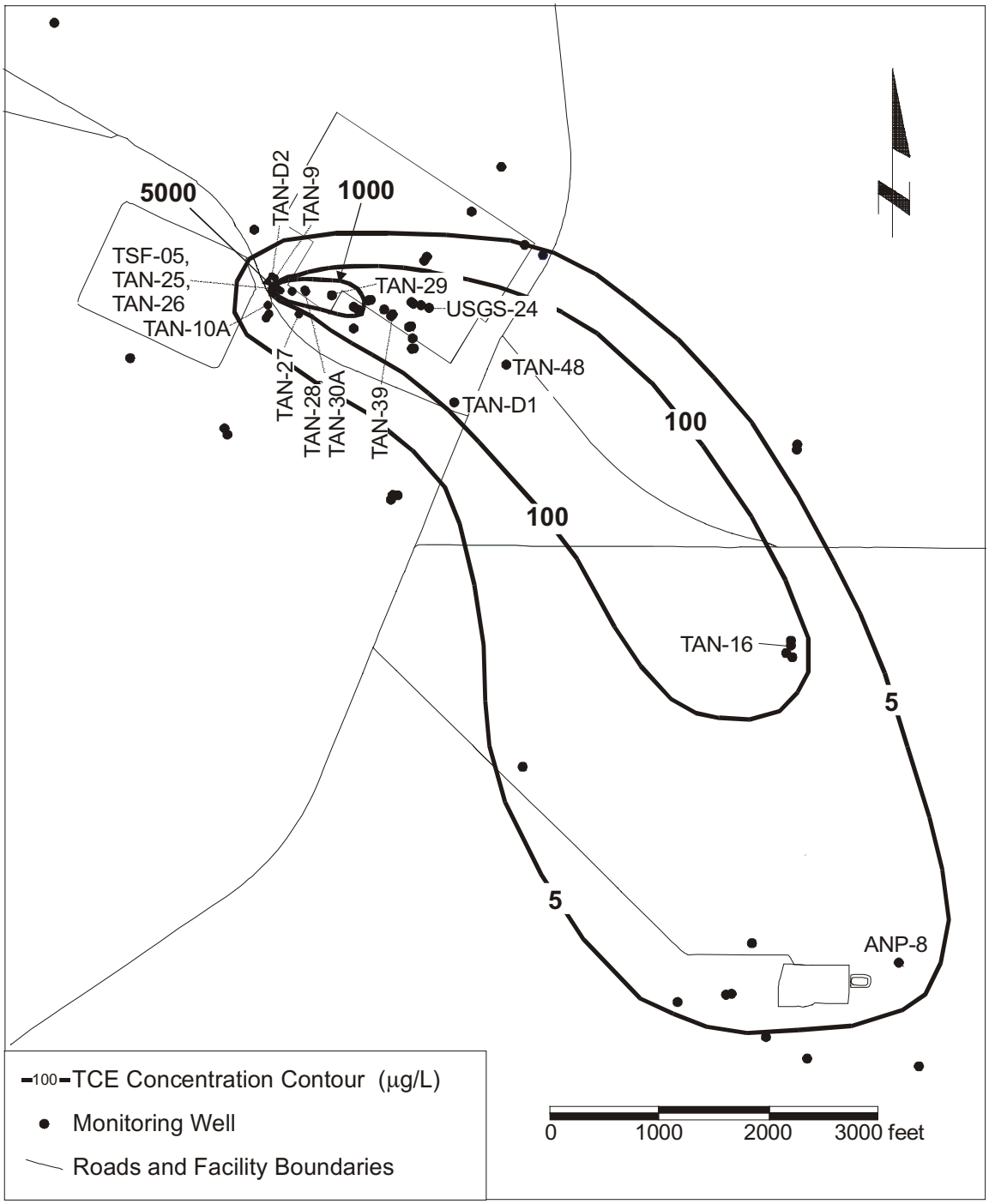

Figure 1. The Test Area North TCE plume.

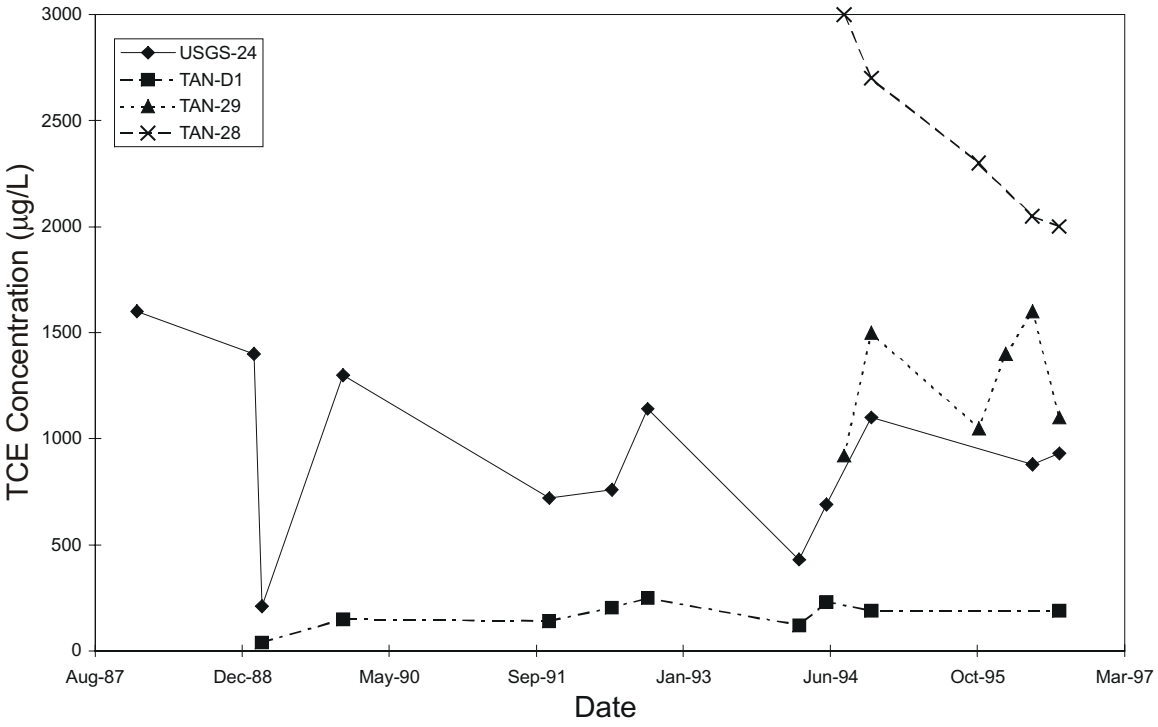

Figure 2. History of TCE concentrations at wells in the upgradient portion of the TAN plume.

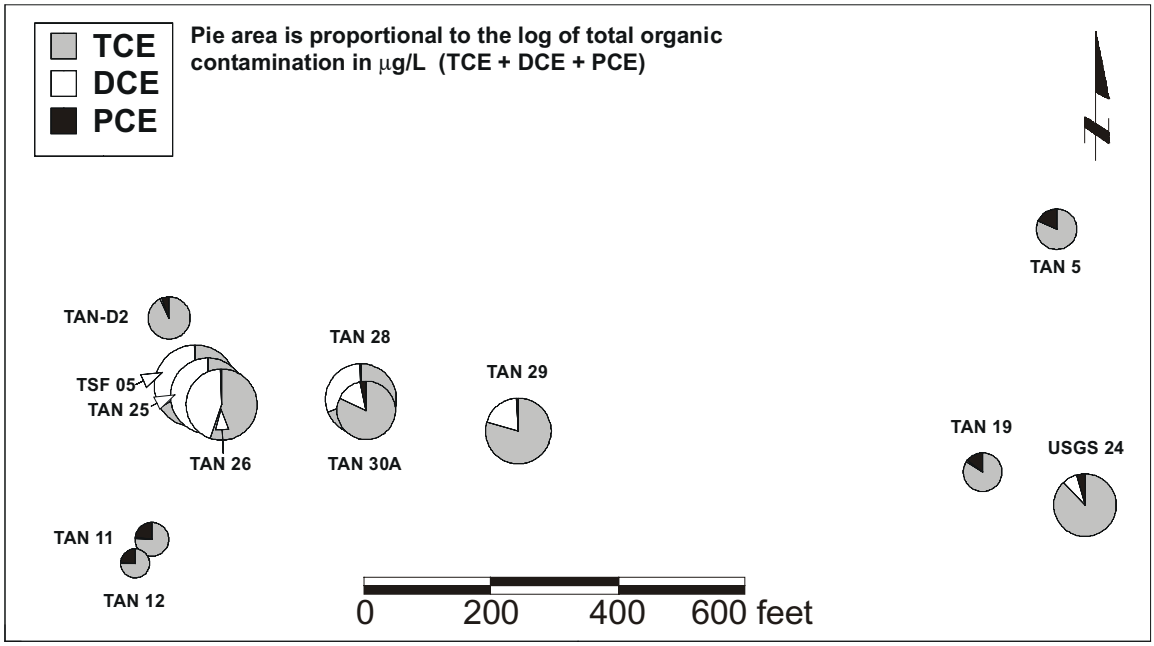

Figure 3. Distribution of chloroethenes near Well TSF-05.

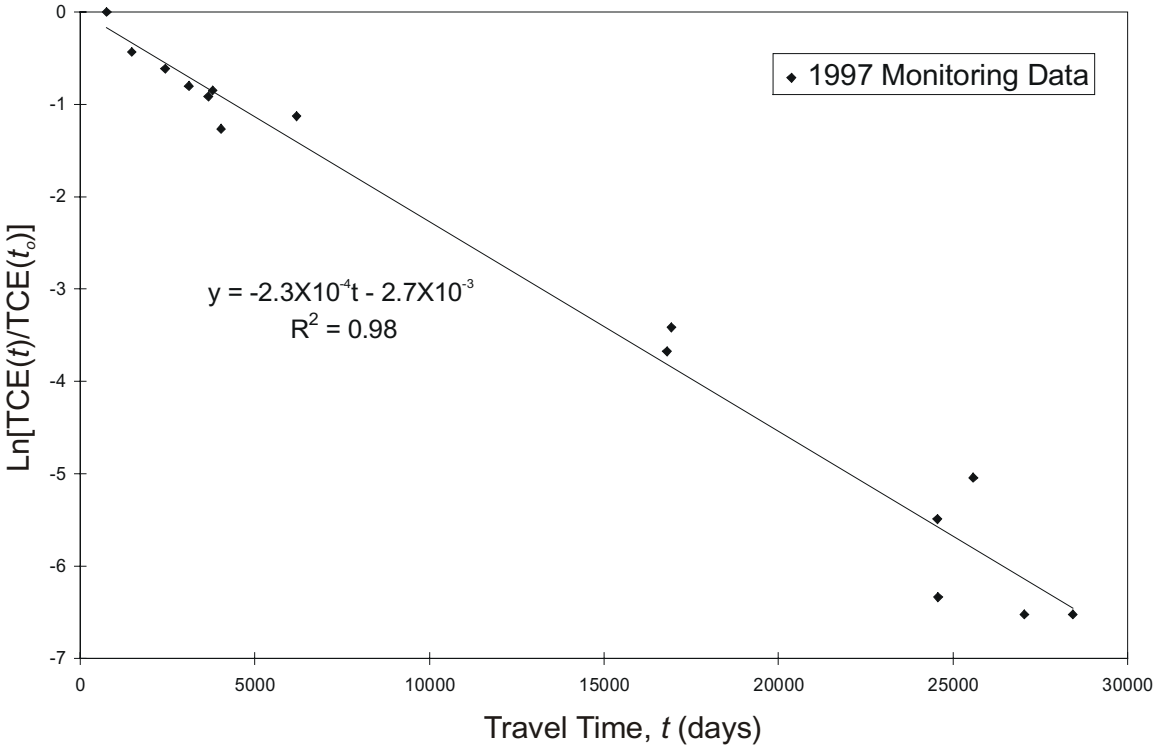

Figure 4. Graphical extraction of gross first-order TCE attenuation rate.

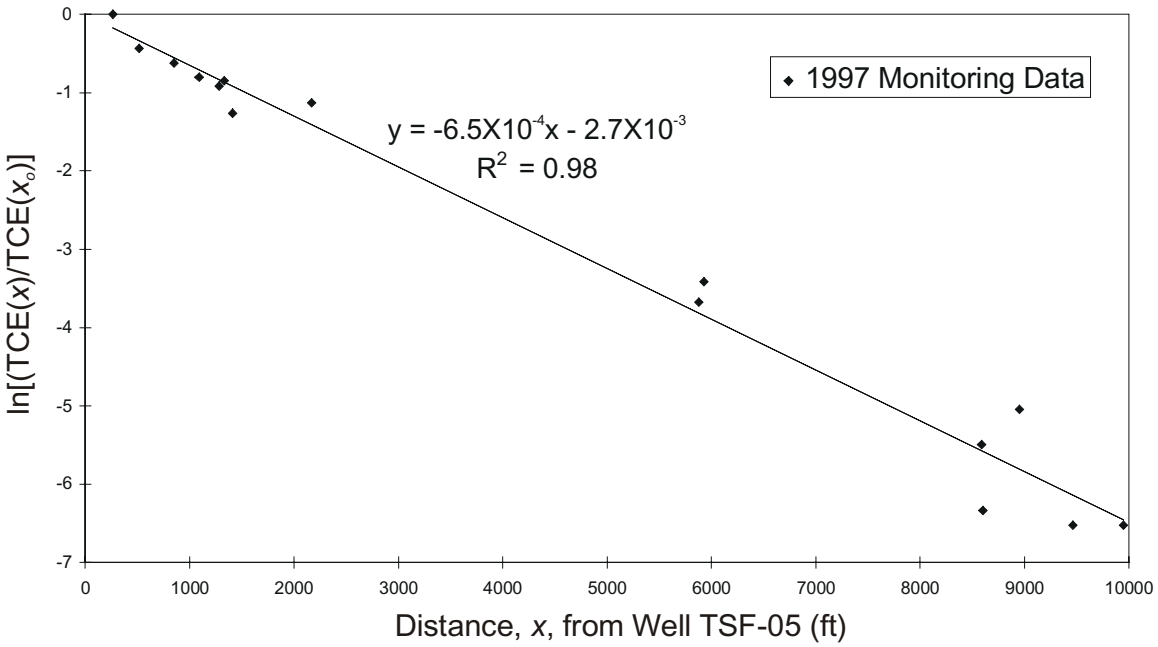

Figure 5. Buscheck and Alcantar (1995) method for estimating first-order TCE degradation rate.

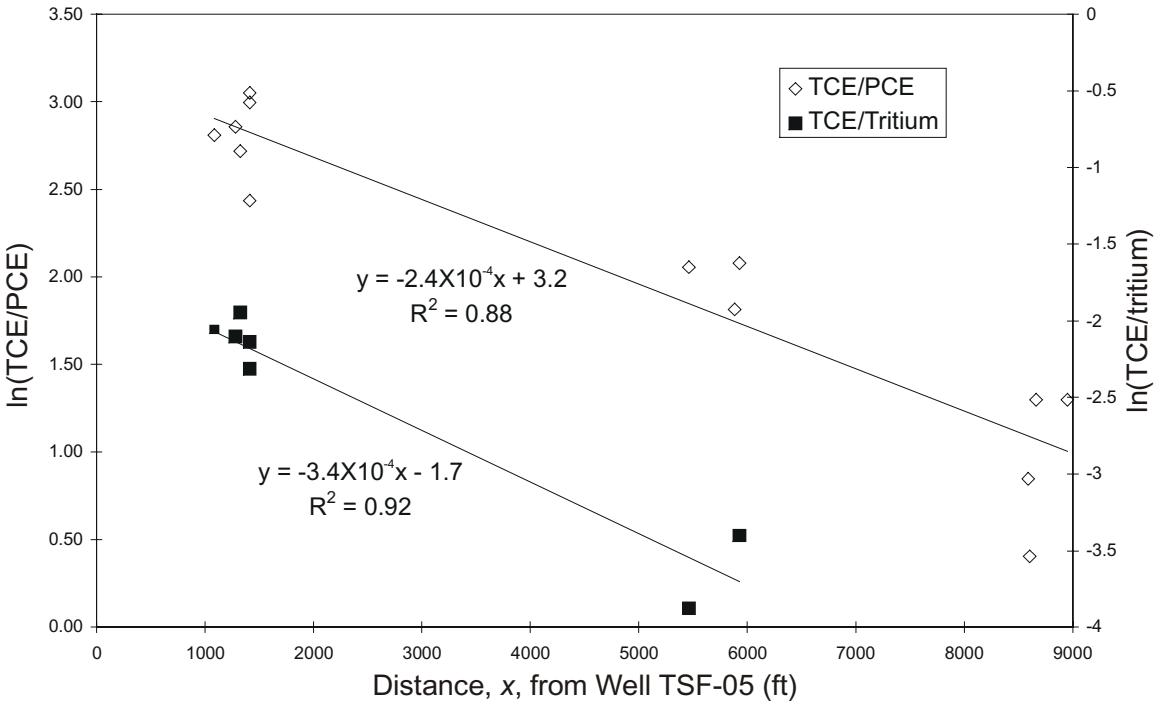

Figure 6. First-order degradation rate estimation using tracer-corrected TCE concentrations.

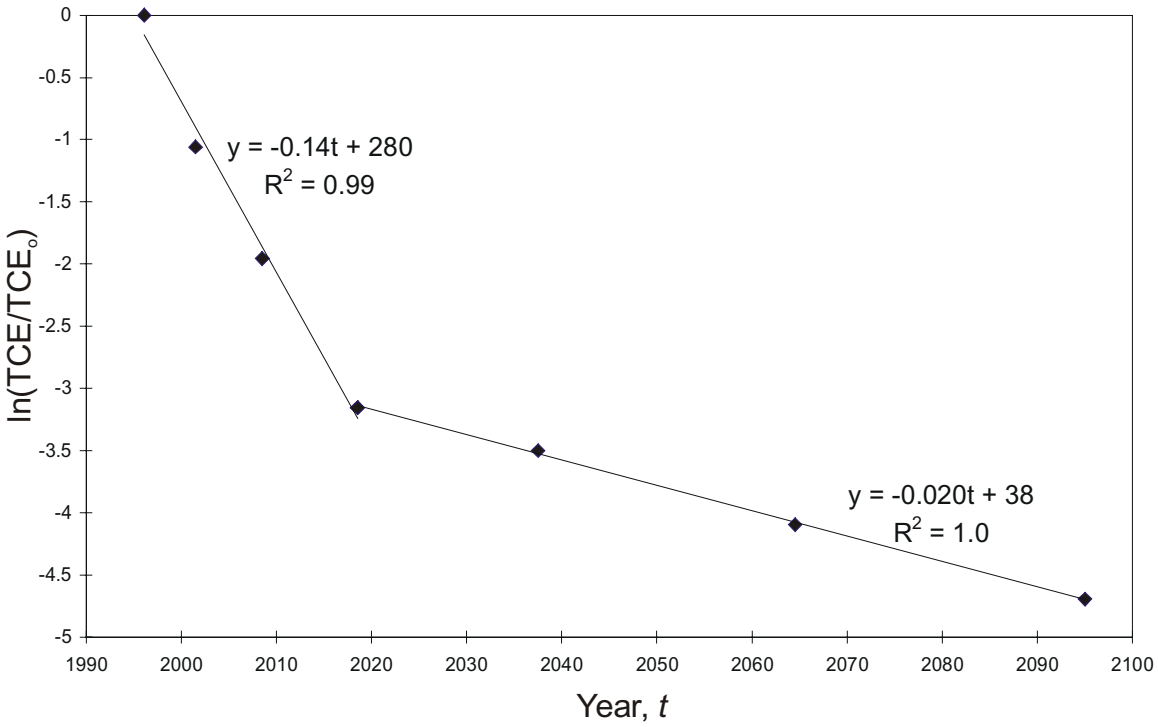

Figure 7. Simulated maximum TCE concentration decline due to dispersion.